Claims

1. A CO_2 sensor comprising a pH indicator and a long-lived reference luminophore, the reference luminophore either being doped in sol-gel particles and co-immobilised with the pH indicator in a porous sol-gel matrix, or being immobilised in a separate oxygen impermeable layer and the pH indicator in a sol-gel matrix being laid over the impermeable layer.

2. A CO_2 sensor as claimed in claim 1 wherein the pH indicator is selected from the group consisting of pH indicators including hydroxypyrene trisulphonate (HPTS), fluorescein, rhodamine B and other fluorescent pH indicators.

3. A CO_2 sensor as claimed in claim 1 or 2 wherein the long-lived reference luminophore is selected from the group consisting of a luminescent complex, in particular [Ru^{II}-tris(4,7-diphenyl-1,10-phenanthroline)]Cl_2, ruthenium-based compounds with α-diimine ligands, luminescent transition metal complexes with platinum metals Ru, Os, Pt, Ir, Re or Rh as the central metal atom and with α-diimine ligands, and phosphorescent porphyrins with Pt or Pd as the central metal atom or luminescent doped crystals such as manganese-activated magnesium fluorogermanate, ruby, alexandrite and Nd-Yag.

4. A CO_2 sensor as claimed in any preceding claim wherein the porous sol-gel matrix is selected from the group consisting of a methyltriethoxysilane (MTEOS) sol-gel matrix, hybrid (organic-inorganic) sol-gel matrices including ethyltriethoxysilane (ETEOS), phenyltriethoxysilane (PhTEOS), n-octyl TEOS and methyltrimethoxysilane (MTMS), and UV-curable sol-gels, soluble ormosils, or hybrid polymer matrices.

5. A CO_2 sensor as claimed in any preceding claim wherein the luminophore is a ruthenium-doped sol-gel particle, in particular [Ru^{II}-tris(4,7-diphenyl-1,10-phenanthroline)]Cl_2. -doped particles.

6. A CO_2 sensor as claimed in any preceding claim wherein the pH indicator and the long-lived reference luminophore are co-immobilised in a sol-gel matrix.

7. A combined O_2 /CO_2 sensor comprising:-

(a) an O_2 sensor comprising an oxygen sensitive luminescent complex immobilised in a porous sol-gel matrix, and

(b) an CO_2 sensor comprising a pH indicator and a long-lived reference luminophore, the reference luminophore either being doped in sol-gel particles and co-immobilised with the pH indicator in a porous sol-gel matrix, or being immobilised in a separate oxygen impermeable layer and the pH indicator in a sol-gel matrix being laid over the impermeable layer.

8. A combined O_2 /CO_2 sensor wherein the pH indicator and the long-lived reference luminophore are co-immobilised in a porous sol-gel matrix.

9. A combined O_2 / CO_2 sensor as claimed in claim 8 wherein the ruthenium-complex is selected from the group consisting of an oxygen sensitive luminescent complex such as ruthenium-based compounds with α-diimine ligands and luminescent transition metal complexes with platinum metals (Ru, Os, Pt, Ir, Re or Rh) as the central metal atom and with α-diimine ligands, and phosphorescent porphyrins with Pt or Pd as the central metal atom or luminescent doped crystals such as manganese-activated magnesium fluorogermanate, ruby, alexandrite and Nd-Yag.

10. A combined O_2 / CO_2 sensor as claimed in claim 8 or claim 9 wherein the immobilised O_2 sensor and the immobilised CO_2 sensor are coated onto the same substrate.

11. A combined O_2 / CO_2 sensor as claimed in claim 8 to 10 wherein the two sensors are coated onto the substrate side-by-side.

12. A combined O_2 / CO_2 sensor as claimed in any of claims 5 to 8 wherein the substrate is selected from the group consisting of plastics materials including surface-enhanced PET, PE and PET/PE laminates, adhesive plastic labels, rigid substrate

materials including glass, Perspex/PMMA, polymer materials from which DVDs are made for example polycarbonate and other polymer materials, metal, and flexible substrate materials including acetate or flexible polymer materials, paper, optical fibre or glass/plastic capillary tubes.

13. A method of making a CO_2 sensor comprising :-
(1) synthesis of an $Ru(dpp)_3(TSPS)_2$ ion-pair comprising mixing dissolved $Ru(dpp)_3Cl_2$ with trimethylsilylpropane sulfonic acid, sodium salt and allowing the ion-pair to precipitate,
(2) synthesis of the particles comprising condensing the dissolved $Ru(dpp)_3(TSPS)_2$ ion-pair with TEOS and halting the condensation reaction with alcohol, washing the condensate with alcohol and drying the condensate, and
(3) and fabrication of the CO_2 sensor films comprising either (a.) suspending the doped reference particles in the coimmobilisation matrix solution, mixing the coimmobilisation matrix solution into a pH indicator solution which comprises a pH indicator in a quaternary ammonium hydroxide solution, and saturating the mixture immediately with CO_2 followed by deposition onto a substrate or (b.) a dual-layer configuration where a low oxygen-sensitivity ruthenium complex is sealed in an oxygen impermeable layer and over-coated with the HPTS-based CO_2 sensing layer.

14. A method as claimed in claim 13 wherein the quaternary ammonium hydroxide is selected from the group consisting of cetyl-trimetyl ammonium hydroxide (CTA-OH), tetra-octyl ammonium hydroxide (TOA-OH) or tetra-butyl ammonium hydroxide (TBA-OH) or other quaternary ammonium hydroxides.

15. A method as claimed in claim 13 or 14 wherein the pH indicator is selected from the group consisting pH indicators including hydroxypyrene trisulphonate (HPTS), fluorescein, rhodamine B and other fluorescent pH indicators.

16. A packaging medium having a combined CO_2 sensor and an O_2 sensor as claimed in any of claims 8 to 12 formed on a surface of the medium which will lie internally of the package when the package is formed.

17. A packaging medium as claimed in claim 16 wherein the sensors are formed on the packaging medium by a method selected from the group consisting of dip-coating, spin-coating, spray-coating, stamp-printing, screen-printing, ink-jet printing, pin printing, lithographic or flexographic printing or gravure printing.

18. A quality control method comprising reading a combined O_2 / CO_2 sensor as claimed in any of claims 8 to 12, formed on the internal surface of a package, with an optical reader, and determining the levels of O_2 and CO_2 inside the package in relation to a control.

19. A method of screen-printing a combined O_2 /CO_2 sensor as claimed in any of claims 8 to 12 onto a substrate comprising forcing the sensor sol through a mask or mesh and drying the substrate.

20. A method of ink-jet printing a combined O_2 /CO_2 sensor as claimed in any of claims 5 to 9 onto a substrate comprising filling an ink reservoir of an ink-jet printer with sensor sol and printing the sensor sol onto the substrate using an ink-jet printer.

21. A method of forming a gas-sensitive sensor on a substrate comprising coating or printing the substrate with a porous sol-gel matrix comprising a gas sensitive indicator.

22. A method as claimed in claim 21 wherein the gas sensitive indicator is an oxygen-sensitive luminescent complex.

23. A method as claimed in claim 21 wherein the gas sensitive indicator is a pH indicator and a long-lived reference luminophore.

24. A method as claimed in claim 21 wherein the gas sensitive indicator is a pH indicator and the substrate is further provided with separate oxygen impermeable layer comprising a long-lived reference luminophore.

25. A method as claimed in any of claims 21 to 23 wherein two gas sensors are formed on the substrate.

26. A method as claimed in any of claims 21 to 25 wherein the sensor is formed on the substrate by a method selected from the group consisting of dip-coating, spin-coating, spray-coating, stamp-printing, screen-printing, ink-jet printing, pin printing, lithographic or flexographic printing or gravure printing.

27. A method as claimed in any of claims 21 to 26 wherein the substrate is selected from the group consisting of plastics materials including surface-enhanced PET, PE and PET/PE laminates, adhesive plastic labels, rigid substrate materials including glass, Perspex/PMMA, polymer materials from which DVDs are made for example polycarbonate and other polymer materials, metal, and flexible substrate materials including acetate or flexible polymer materials, paper, optical fibre or glass/plastic capillary tubes.

28. A method as claimed in any of claims 21 to 27 wherein the sensor is a luminophore-based sensor.

29. A method as claimed in any of claims 21 to 27 wherein the sensor is a colorimetric-based sensor.

30. A substrate having a gas-sensitive sensor formed thereon wherein the sensor comprises a sol-gel matrix comprising a gas sensitive indicator and the sensor has been formed by printing or coating.

31. A substrate as claimed in claim 30 wherein the substrate is selected from the group consisting of plastics materials including surface-enhanced PET, PE and PET/PE laminates, adhesive plastic labels, rigid substrate materials including glass, Perspex/PMMA, polymer materials from which DVDs are made for example polycarbonate and other polymer materials, metal, and flexible substrate materials including acetate or flexible polymer materials, paper, optical fibre or glass/plastic cap.